

NASA Technical Paper 2715

April 1987

The Corrosion Mechanisms for Primer Coated 2219-T87 Aluminum

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and Ward W. Knockemus

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**Scientific and Technical
Information Branch**

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TECHNICAL PAPER

THE CORROSION MECHANISMS FOR PRIMER COATED 2219-T87 ALUMINUM

INTRODUCTION

Electrochemical methods for estimating corrosion rates of bare and painted metal surfaces serve as effective accelerated approaches to scientific techniques of corrosion studies. For at least 15 years, direct current (DC) methods, particularly polarization resistance, have permitted quick determination (30 to 60 min) of corrosion currents that translate into mils per year of metal surface corroding.

Within the past six to eight years, alternating current (AC) methods, particularly AC impedance scans of metals in corrosive solution environments, have resulted in studying the corrosion system in more detail. The several data from a typical AC impedance scan can indicate change in corrosion rate, progressive deterioration of metal coatings, changes in metal surface, and reaction mechanisms. Moreover, changes in coating condition can be detected by AC experiments before DC methods show an increase in metal corrosion current.

However, the AC impedance study of corroding metals is in its infancy. A few dozen papers describe AC corrosion studies, but clear interpretation of the data is rare and stated conclusions are sometimes unsupported or untrue. A review of the field is needed to sort out the complex data obtained and to indicate what conclusions are justified. A standard treatment of the most useful data from the typical AC impedance experiment needs to be indicated. So the researcher in this field has to be ready to blaze trails with thoughtfulness, imagination, and patience.

Nevertheless, the reader should consider two papers that provide useful background [1,2]. Anyone interested in the field should begin with AC studies of bare metal surfaces that produce data more easily analyzed and understood. Coated surfaces yield data much more complex and challenging to unravel.

This work was undertaken primarily to evaluate the role of the AC Impedance Method in the study of aluminum corrosion beneath primer coated surfaces. Its applicability to the space program therefore concerns both the External Tank and Solid Rocket Boosters of the Space Shuttle Transportation System. The present study incorporates both the AC Impedance Method and a DC Method (Polarization Resistance), and an attempt is made to correlate the results from both methods.

BACKGROUND

A thorough study of the mechanism of aluminum corrosion has been made by Boies and McDonald [3]. The mechanism of corrosion inhibition by zinc chromate primers involves polarization of cathodic sites by precipitation of a complex material, such as zinc chromate or zinc tetroxy chromate to slow corrosion, preventing the spread of corrosion and allowing natural processes to heal the anodic site. An article on the same subject has been published by Danford and Higgins [4].

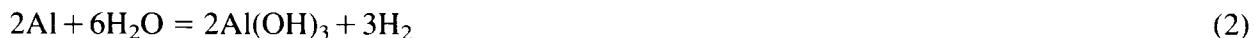
For the corrosion of aluminum, the painted aluminum may be considered as a voltaic cell, with the aluminum metal as the anode, separated from the paint film, which acts as the cathode compartment, by an inner layer of amorphous Al_2O_3 and an outer layer of crystalline hydroxide, probably $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ at room temperature. The outer bulk layer is porous and does not afford protection, while the thickness of the layer of amorphous aluminum oxide is the controlling factor in the corrosion process. Electrons pass across the barrier fairly readily, but the diffusion of aluminum ions across this layer is slow. According to Boies and McDonald, growth of the barrier layer stops at a thickness depending on the driving force or cell potential E_{CELL} . Aluminum may corrode in two ways. For the first way, the overall chemical reaction is:



for which

$$E_{\text{CELL}} = 2.06 + 0.0148 \log [\text{O}_2]$$

The second possible reaction is:



for which

$$E_{\text{CELL}} = 0.832 \text{ V}$$

Thus, as the concentration of oxygen decreases in reaction (1), the primary reaction, reaction (2) becomes more dominant and is known as the hydrogen evolution reaction. Since this reaction occurs at a lower voltage, where the thickness of the barrier layer is small, it is much more rapid than reaction (1). This was verified by an experiment involving the DC polarization resistance method, in which the corrosion rate of Al was measured during an air purge of the medium (corrosive H_2O) as 0.3 mils/year. The solution was then purged with nitrogen to remove oxygen, and the corrosion rate was 3.2 mils/year, a large rate increase.

The initial reaction, therefore, proceeds according to reaction (1), slowed by the presence of inhibitors. The rate is most likely limited by the diffusion of oxygen to the cathodic sites. As long as oxygen is available, reaction (1) proceeds normally, while the thickness of the barrier layer remains constant, unless disturbed by other factors such as the nature of the medium. It was a purpose of the present work to determine this influence through study of samples immersed at both pH 5.5 and pH 8.2 (Al_2O_3 is soluble in either acids or alkalis). The overall rate of reaction (1) is probably governed by the rate of decrease in oxygen concentration as well as the rate of thinning of the barrier layer, due either to dissolution by the electrolyte solution or to a decrease in cell voltage or both.

AC IMPEDANCE THEORY

Impedance Basics

For alternating current flow, Ohm's Law has the form $E = IZ$, where Z is impedance in ohms and E and I are waveform amplitudes of voltage and current, respectively. Impedance, the resistance within an AC circuit to electron movement, is caused by circuit elements such as resistors, capacitors, and inductors. Impedance can affect not only the current waveform at a fixed voltage, but also can alter time-dependent characteristics of the current or voltage waveform with respect to each other. The separation of voltage and current waves that can occur in reactive circuits is called phase or phase shift and is expressed in degrees. Phase depends on circuit elements, their arrangement and the AC frequency. In fact, a phase versus frequency plot is characteristic of a given circuit. No phase shift occurs with only resistances in an AC circuit, but the presence of a capacitor can cause the voltage to lag the current wave by as much as 90 deg.

The total impedance $|Z|$ at a given frequency depends on resistive and capacitive contributions. Total impedance can be represented by a vector $|Z|$ with a real component Z' , and an imaginary component $-Z''$.

Hence,

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2} \quad (1)$$

and

$$\tan \theta = - \frac{Z''}{Z'} \quad (2)$$

where θ is the phase shift of the resulting current with respect to the applied voltage.

At sufficiently high frequencies, capacitors contribute little to the total impedance in an AC circuit. A plot $-Z''$ (often called imaginary impedance) versus Z' (often called real impedance) is termed a "complex

plane plot" or Nyquist plot. In a Nyquist plot from a corroding metal surface, the highest frequency points begin on the horizontal Z' axis at a distance from the $-Z''$ axis proportional to the combined solution and coating layer (if present) resistances.

Capacitors

A capacitor is a simple device capable of storing electric charges at some potential difference. Often a capacitor (or condenser) consists of two solid metal surfaces separated by a dielectric, but a single charged metal surface dipping in a polar solvent (like water) functions as a capacitor because a "double layer" forms.

The double layer consists of excess electrons near the metal surface separated from a rigid layer of hydrated cations by a monolayer of polar water molecules. The electron layer and the cation layer are also labeled Helmholtz Double Layer; it is strictly analogous to the parallel plate condenser (PPC). If the electrode is charged positively, the orientation of water molecules reverses and the counter ion monolayer is composed of anions. The capacitance C in farads equals the charge build-up Q , in coulombs per volt of potential difference V , $C = Q/V$. The capacitance of a PPC is increased by a factor K if an insulator with dielectric constant K is placed between the plates. $K = 1$ for a vacuum; for a completely oriented monolayer of water molecules on an electrode surface $K = 6$ [5]. Also, the capacitance of a PPC is inversely proportional to the distance between plates assuming no change in the dielectric constant of the insulator.

A protective coating can take on capacitive properties in an electrolyte solution if it becomes porous to permit water and charge build-up on either side of its surface. A conductive coating like zinc chromate would not show capacitance like that of an organic polymer, although if a conductive coating absorbs water it would increase in capacitance. Porous metal oxide coatings should also show capacitance although this has not been clearly demonstrated.

The charging or discharging of a capacitor in an AC circuit is driven by the applied voltage and its polarity. The charging time for a capacitor in series with a resistor depends on its capacitance, C , in farads and the resistance, R in ohms of the resistor. $R \times C$ is called the time constant; in five time constants such a capacitor is over 99 percent charged. Obviously if the AC frequency is greater than five times constants, a circuit capacitor cannot fully charge or discharge.

The Equivalent Circuit Concept

The basis of the AC impedance methods is the modeling of the corrosion cell in terms of a purely electronic circuit model. This model consists of one or more resistors and capacitors in a suitable arrangement. The equivalent circuit is designed to mirror the electronic behavior of the corrosion cell in the most accurate manner possible.

A corroding bare metal surface in aqueous solution shows resistance R_t to electron flow and its electrical double layer shows capacitance C_{dl} . If the solution has resistance R_{Ω} , then the equivalent circuit can be represented as shown in Figure 1. A suitable equivalent circuit should reasonably reproduce experimental plots obtained from the corrosion cell when experimentally determined parameters are used. These

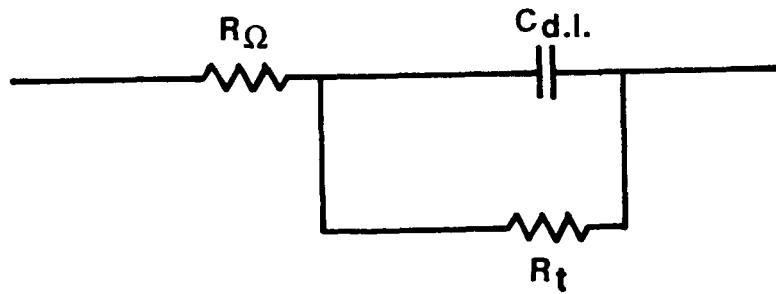


Figure 1. Circuit representing AC Impedance response for bare metals.

plots include the Bode phase (degrees versus $\log W$, where $W = 2\pi X$ frequency) and the complex plane or Nyquist plot ($-Z''$ versus Z').

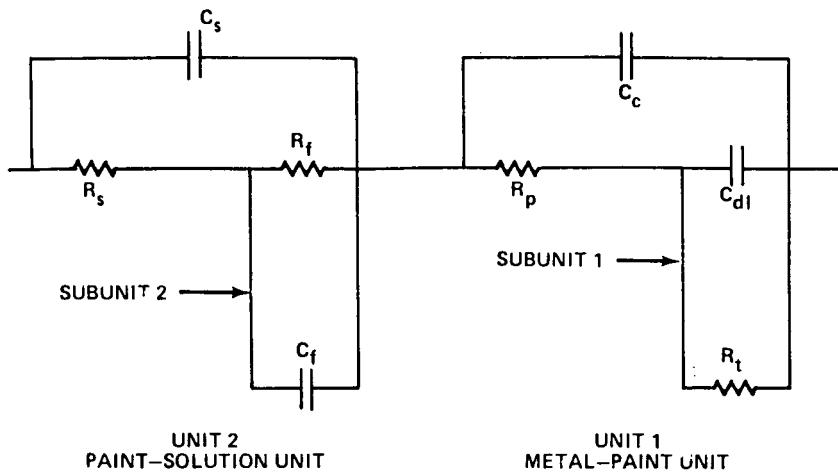
Equivalent circuits for coated metal surfaces involve additional capacitor-resistor combinations. Such a circuit that fits corroding zinc chromated aluminum is shown in Figure 2. It also must display similar Bode and Nyquist plots that resemble the experimental data plots. It should be pointed out that these plots can vary between similarly prepared samples and can change as corrosion and coating deterioration progresses.

AC DATA ANALYSIS

The goals of analyzing AC impedance data are threefold: (1) determine the equivalent circuit that most accurately describes the corrosion cell; (2) assign the best possible values to resistors and capacitors in the equivalent circuit for that particular experiment (experiments should be run every 2 days for about 4 weeks or until the corrosion rate stabilizes or the coating visibly deteriorates); and (3) discover the best parameters in the equivalent circuit to describe the corrosion rate. As sample immersion continues, all of the model parameters change, some more than others.

The starting point in deciphering the experimental results is the Nyquist or complex plane plot. Points on this plot correspond to changing $-Z''$, Z' values as the signal frequency changes during a typical scan from 10^{-2} to 10^5 Hz. Usually the Nyquist plot consists of one semicircle for a corroding bare metal and two semicircles (often one and one-half) for a coated metal. Theoretical origin of the data points that approximate a semicircle is discussed in Reference 1. One capacitance and two resistances are obtained from each semicircle.

This simple plot is obtained for a corroding bare metal surface which has the equivalent circuit given earlier. Reading Z' from the plot at frequency W_{\max} enables calculation of $C_{d.I.}$. R_Ω and R_t are estimated by linear measurement along the Z' axis. In practice a least squares computer calculation for these equivalent circuit parameters gives the best values. Input values are from linear measurements of Nyquist semicircles. Similarly a second semicircle which lies to the right of the first in the Nyquist plot for a coated metal surface yields two more resistance and one more capacitor parameters.



C_s	SOLUTION CAPACITANCE
R_s	SOLUTION RESISTANCE
C_f	FARADAIC CAPACITANCE (COATING/SOLUTION)
R_f	FARADAIC RESISTANCE
C_c	COATING CAPACITANCE
R_p	COATING RESISTANCE
C_{dl}	METAL/COATING INTERFACE CAPACITANCE
R_t	CHARGE TRANSFER RESISTANCE

Figure 2. Circuit representing AC Impedance response for primer coated 2219-T87 aluminum.

At this point in the research of primer coated aluminum corroding in salt water, the equivalent circuit that best fits the experimental data was determined to be that shown in Figure 2. A complex least squares program, based on an adaptation of the general non-linear least squares program ORGLS [6], was developed. It gives the best values for the parameters of the equivalent circuit. Input parameters include four resistances and two capacitances obtained from a least squares fitting of the two semicircles (Nyquist Plot) obtained directly from the experiment. The physical model that the equivalent circuit of Figure 2 represents is shown in Figure 3.

The model in Figure 2 was adapted from that used by Cahen and Chen [7], the only addition being the solution capacitance C_s . This addition was necessary to explain the rise in the phase at high frequencies, and gave a better overall fit of the model to the observed data in general. The quality of fit to the Bode magnitude data ($\log |Z|$ versus $\log W$) is shown in Figure 4, and that for the Bode Phase data (θ versus $\log W$), both with and without C_s , in Figure 5. W is defined as $2\pi f$, where f = frequency of the applied voltage.

In practice, the observed data ($\log |Z|$ versus $\log W$) were fitted using the least squares procedure, with the theoretical phase data being calculated from the model using the parameters obtained from the fit of the Bode Magnitude data.

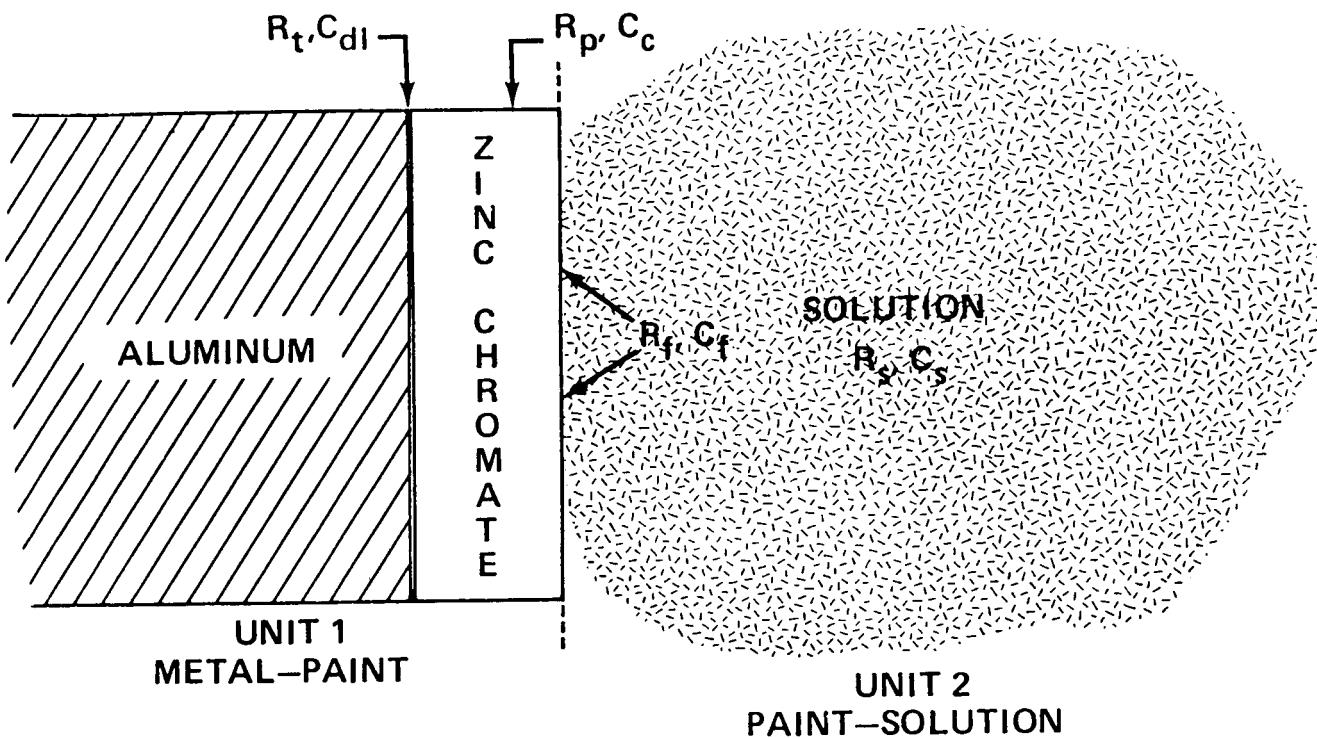


Figure 3. Physical description of circuit parameters for primer coated aluminum.

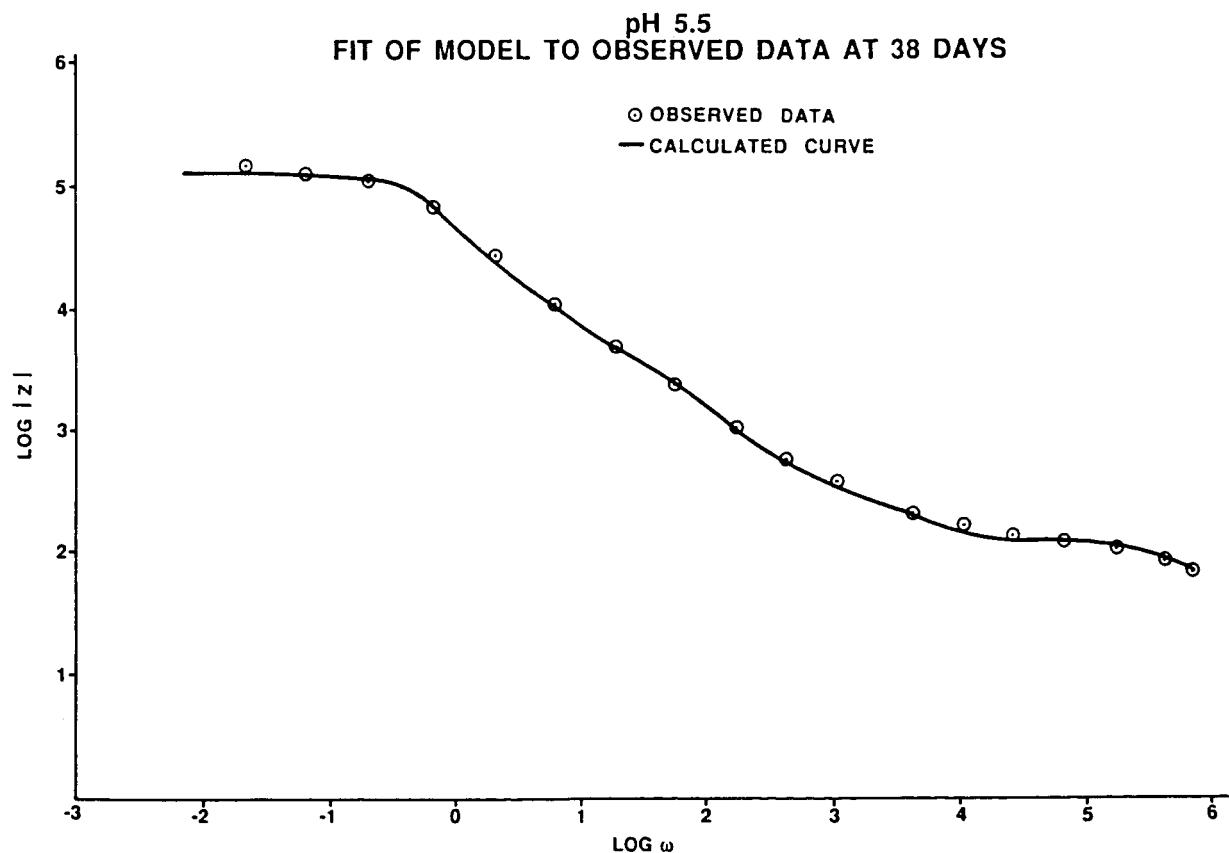


Figure 4. Typical least squares fit of Bode magnitude data.

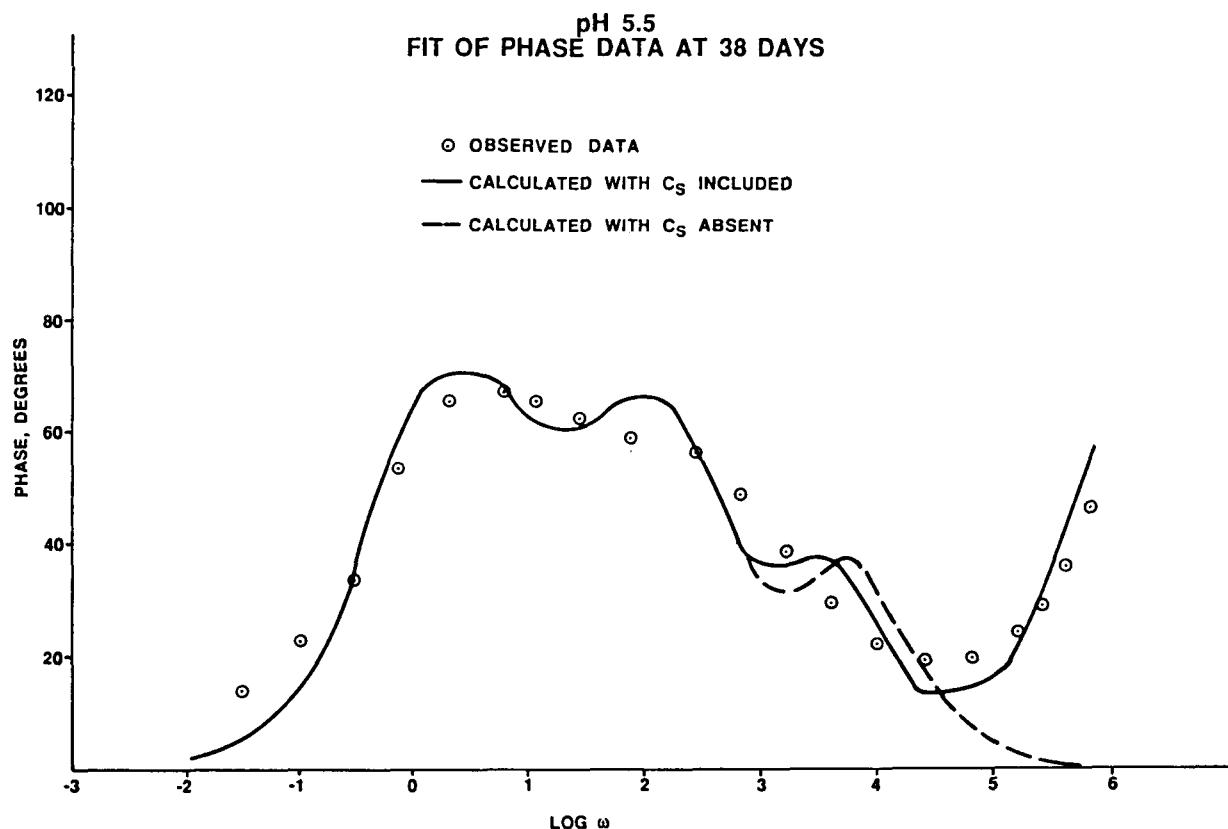


Figure 5. Fit of Bode phase data using parameters obtained from fit of Bode magnitude data.

EXPERIMENTAL

AC impedance and polarization resistance measurements (DC) were made over a period of 40 days each on specimens of 2219-T87 aluminum coated with TT-P-1757 aerosol zinc chromate primer. The aluminum specimens, which were 1.43 cm in diameter and 0.13 cm thick, were coated with primer, allowed to dry, and immersed in 3.5 percent NaCl solution buffered at pH 5.5 and pH 8.2 for the entire period. The sample holder, which exposes a sample area of 1.0 cm to the test solution, is shown in Figure 6.

Sample preparation consisted of a 15 min immersion period of the aluminum specimens in hot alkaline cleaner, followed by a 15 min suspension in Smut-Go chromate deoxidizer. The samples were then treated with Alodine 1200 (conversion coat) for a period of 2 min and sprayed on one side with primer to a thickness of 7.6 μ m (0.3 mil) each.

The EG&G-PARC Model 368 AC Impedance System was used for collection of both the AC Impedance data and the polarization resistance data. Data for each sample were taken on alternate days. AC impedance data were taken in three sections. The first two sections, beginning at 0.001 Hz and 0.1 Hz, were obtained using the Fast Fourier Transform Technique (FFT). The last section, beginning 6.3 Hz and extending to 100,000 Hz, was collected using the Lock-in Amplifier technique. The sequencing was performed automatically using the auto execute procedure, with all data being merged to a single set for each run. The period for collection of the AC impedance data was about 2.5 hr. After collection, the data were processed and analyzed as described previously (Model of Fig. 2).

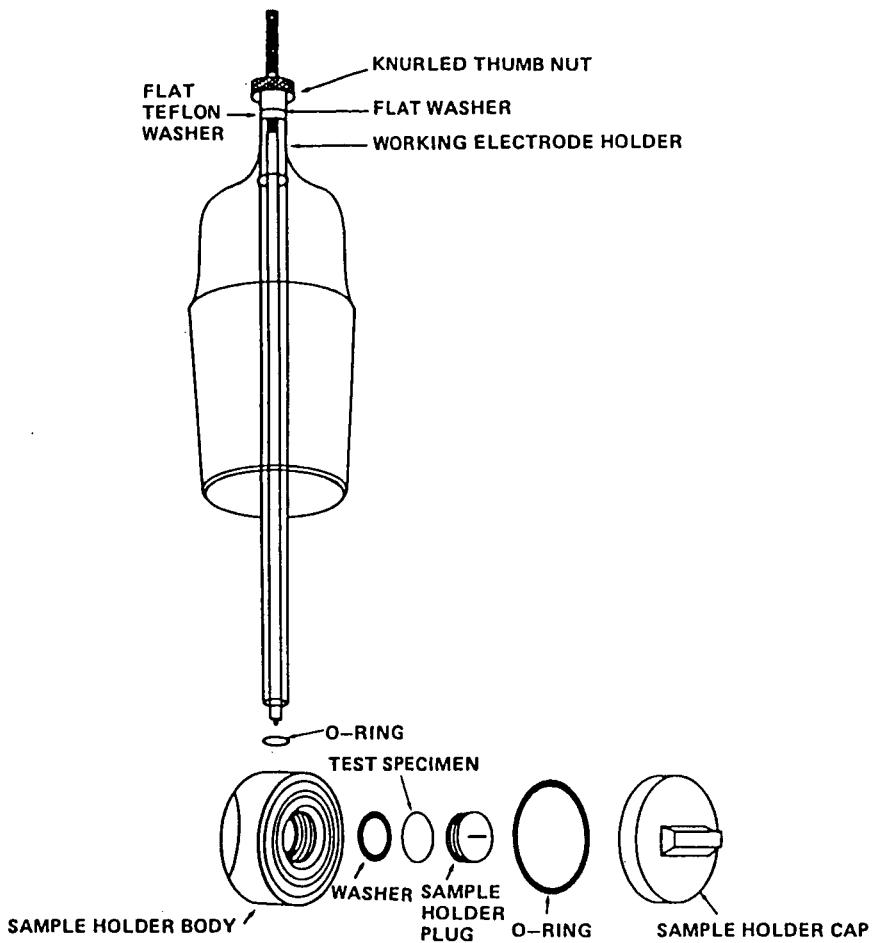


Figure 6. Exploded view of the sample holder.

Data were collected for the polarization resistance method using the same system with the EG&G-PARC Model 332 Corrosion Measurement Software, which was developed especially for DC measurements. The data were automatically corrected during the scan for IR drop using the technique developed by EG&G-PARC. The data were transferred to a larger, faster computer and analyzed using the program POLCURR [8]. The theory for the polarization resistance technique has been described previously [4].

In addition to the foregoing, samples of bare 2219-T87 aluminum were studied at pH 5.5 and pH 8.2 using both the polarization resistance and AC Impedance methods. In these cases, only a single run for each method was made, the AC Impedance data being analyzed according to the model shown in Figure 1.

RESULTS AND DISCUSSION

Bare Aluminum Metal

AC Impedance data were analyzed at pH 5.5 and pH 8.2 using the model shown in Figure 1. At pH 5.5 values of 53 ohms, 11,583 ohms and 5.8 μ F were obtained for R_Ω , R_t , and C_{dl} , respectively. Values of

89 ohms, 11,073 ohms and 12.4 μF were obtained for these parameters at pH 8.2. The corrosion currents, measured using the DC polarization resistance method, were 6.71 $\mu\text{A}/\text{cm}^2$ at pH 5.5 and 3.10 $\mu\text{A}/\text{cm}^2$ at pH 8.2. The corrosion rate for bare aluminum is thus larger at pH 5.5 than at pH 8.2 (about the pH of seawater). Values for the polarization resistance obtained from this method were 785.5 ohms and 1293 ohms at pH 5.5 and pH 8.2, respectively. Thus, contrary to popular belief, the values of R_t obtained with the AC Impedance technique are not the same as the polarization resistance values, but rather represent the resistive contribution to the charge transfer between the metal and surrounding medium. As shown previously [9], the value for R_t is also obtained through the extrapolation of the real part of the impedance to zero frequency. Values for the capacitance C_{dl} indicate that the capacitance is larger at pH 8.2. This may be the result of a thinner barrier layer at pH 8.2.

Primer Coated Aluminum at pH 5.5

The polarization resistance data (I_{CORR} versus time) are shown in Figure 7. As seen from the curve, the corrosion of primer coated Al is cyclic in nature, with peaks attributed to the onset of the hydrogen evolution reaction, with a subsequent thickening of the barrier layer to decrease the corrosion rate.

AC Impedance data were analyzed using the model of Figure 2. There are, therefore, eight parameters, which were fitted by least squares to data sets consisting of 62 points each ($\text{Log } |Z|$ versus $\text{Log } W$). Extrapolation of the linear portion of the Bode Magnitude plots to $W = 0$ clearly showed that the charge transfer mechanism, rather than diffusion, was the rate controlling factor throughout the entire time period. The R_t -time curve is shown in Figure 8. This curve is also cyclic in nature, with minima generally correlating well with maxima in the I_{CORR} -time curve of Figure 7. As stated previously, the AC measurements are more sensitive to changes in the nature of the sample, the DC responses generally lagging the AC responses by about a day. The R_f -time curve (Fig. 9) does not show significant change until the period 22 to 32 days, but the changes are not nearly as large as those in the R_t -time curve. It is significant that the R_p -time curve [Fig. 10(a)] shows maxima in the same region as the R_f -time curve, and indicates that the charge transfer between the primer and solution correlates with a resistance increase within the paint film. The C_f -time curve [Fig. 10(b)] shows little structure, but is generally increasing. The C_s -time curve [Fig. 10(c)], the C_c -time [Fig. 11(b)], and C_{dl} -time curve [Fig. 11(c)] all exhibit maxima in the region 22 to 32 days, showing that the capacitive effect is greater during this period. This results in a shift of capacitive effects to lower frequencies in the plot of $\text{Log } |Z|$ versus $\text{Log } W$, and also changes the shapes of these curves.

Values for the R_n -time curve [Fig. 11(a)] are all small compared to values for the other resistive components, and therefore have a lesser effect on the circuit response. Curves showing the correlation of the total impedance calculated from the model at 1000 Hz with values measured at the same frequency using an AC Impedance Bridge are shown in Figure 12.

Primer Coated Aluminum at pH 8.2

The I_{CORR} -time curve is shown in Figure 13. As with the pH 5.5 curve, this curve is also cyclic in nature, but the shape is different. Values obtained for R_t in the R_t -time curve (Fig. 14) are generally smaller, with smaller changes, than those obtained at pH 5.5, and there is less structure. However, the first minimum in the R_t -time curve at pH 8.2 at about 6 to 7 days corresponds well to the position in the first minimum in the R_t -time curve at pH 5.5. Changes in the R_f -time curve (Fig. 15) are about equal in magnitude to those of the R_t -time curve, and show that the charge transfer between the paint film and solution, as

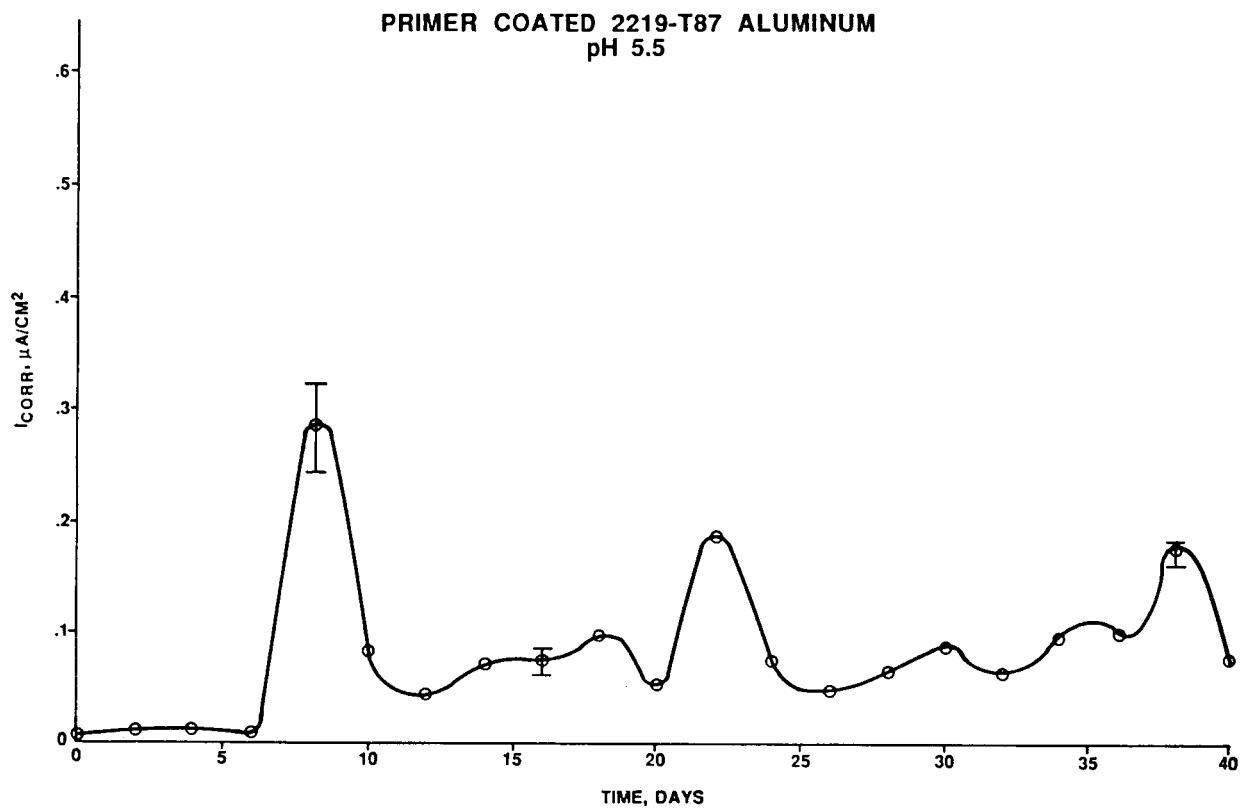


Figure 7. I_{CORR} versus time at pH 5.5 from polarization resistance measurements.

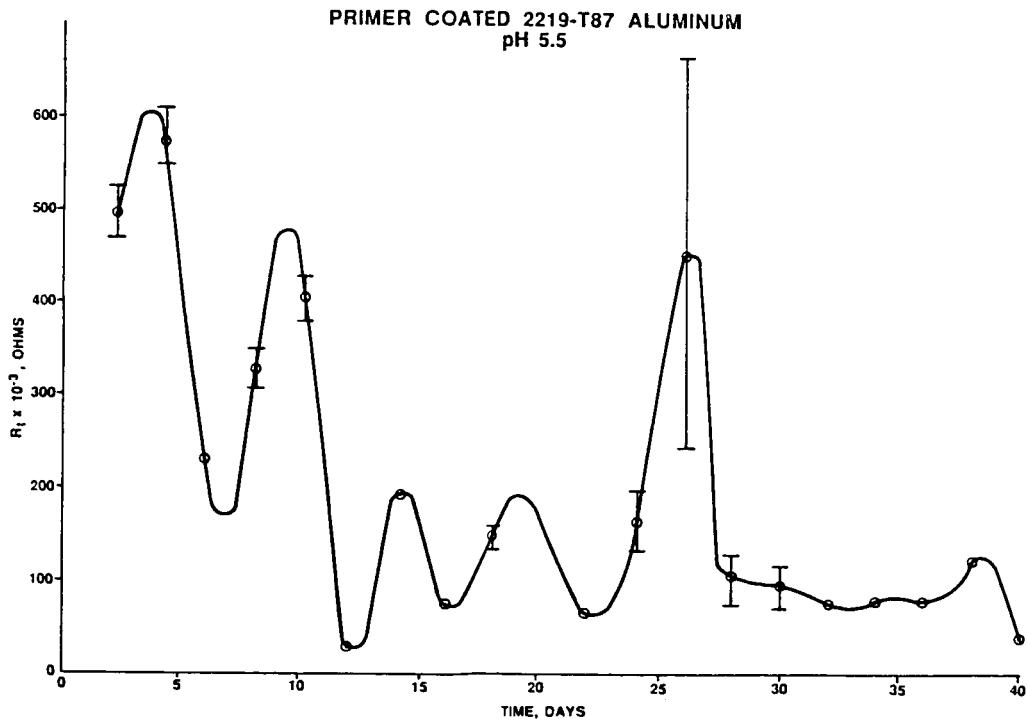


Figure 8. R_t versus time at pH 5.5.

PRIMER COATED 2219-T87 ALUMINUM
pH 5.5

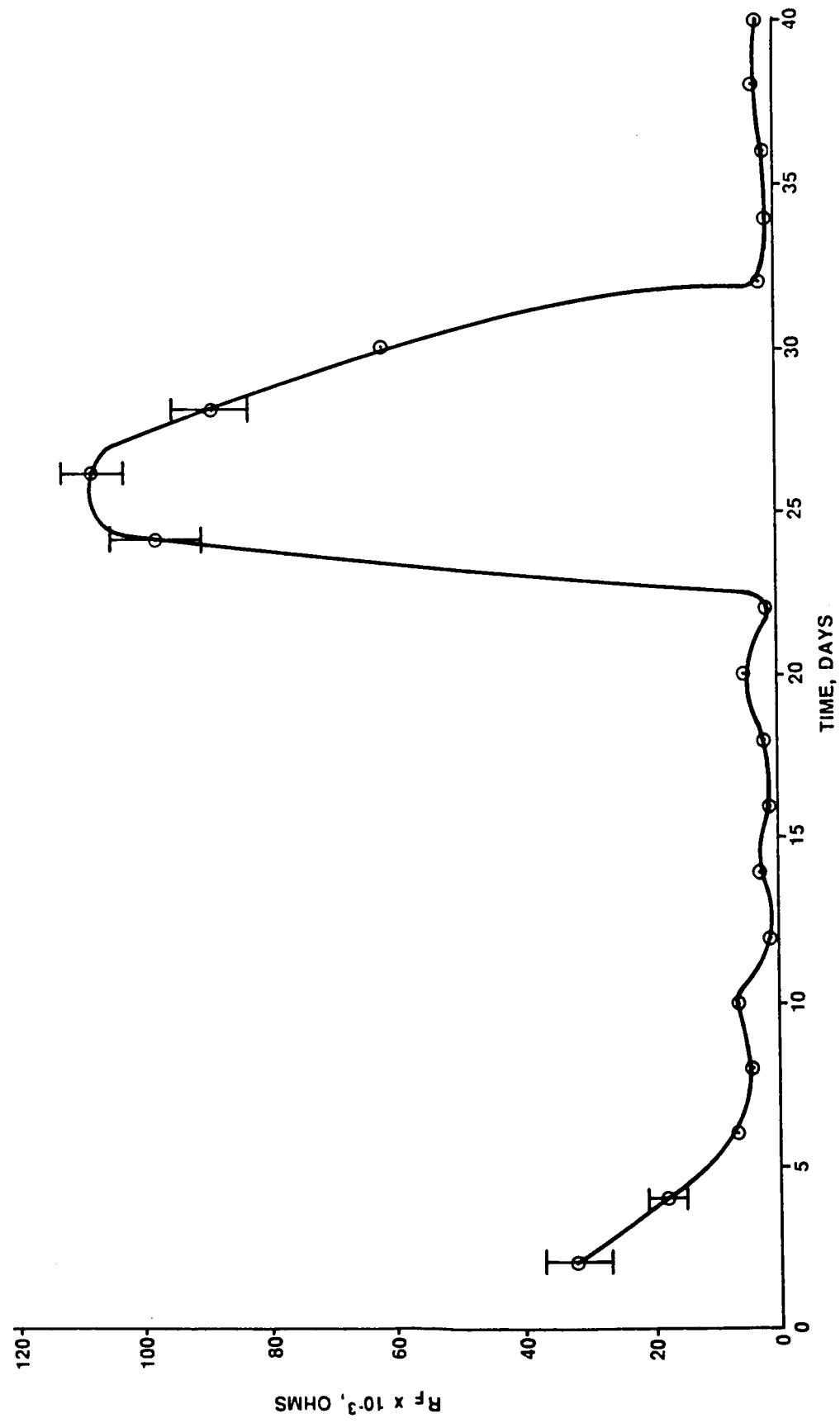


Figure 9. R_f versus time at pH 5.5.

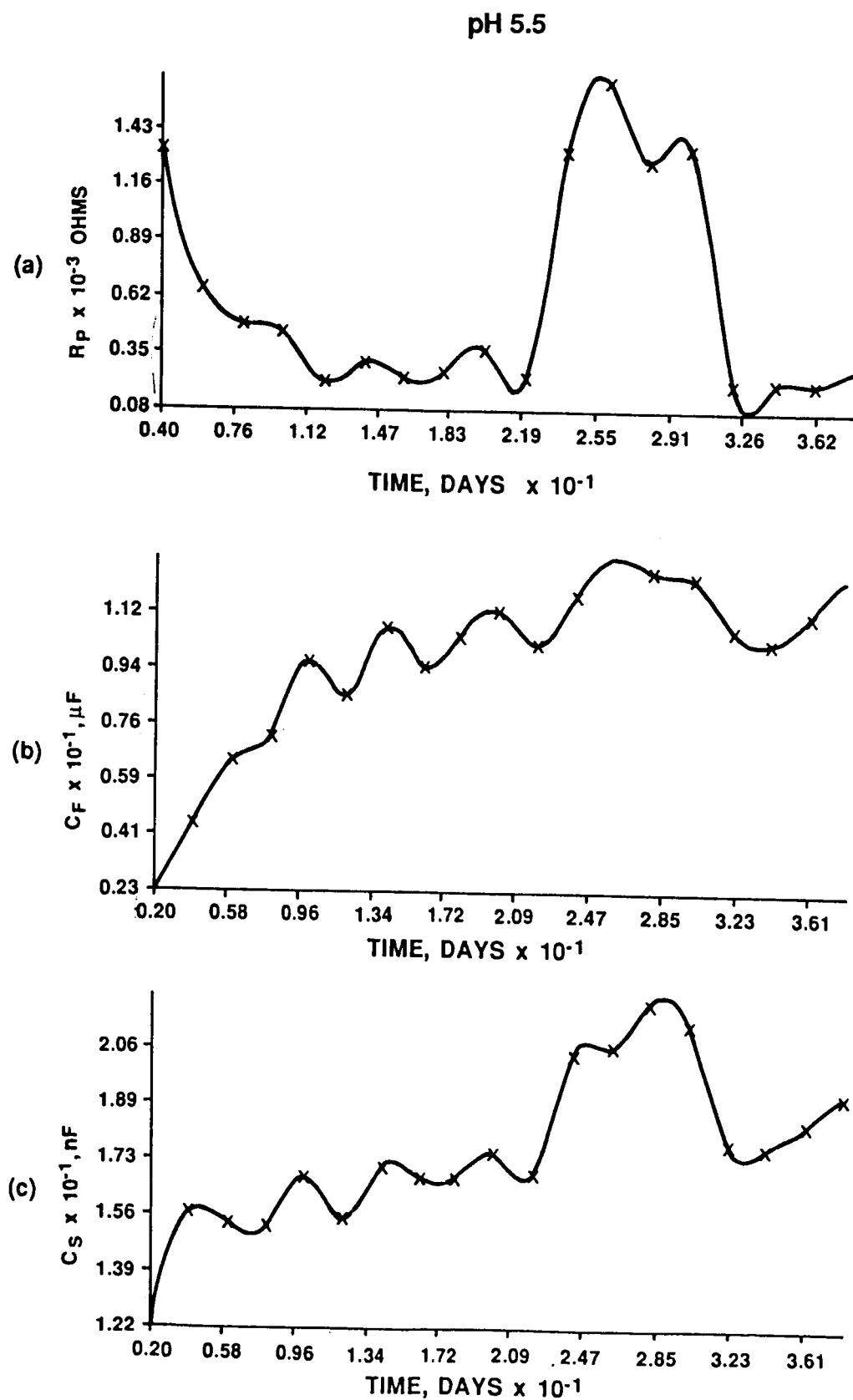


Figure 10. R_p , C_f , and C_s versus time at pH 5.5.

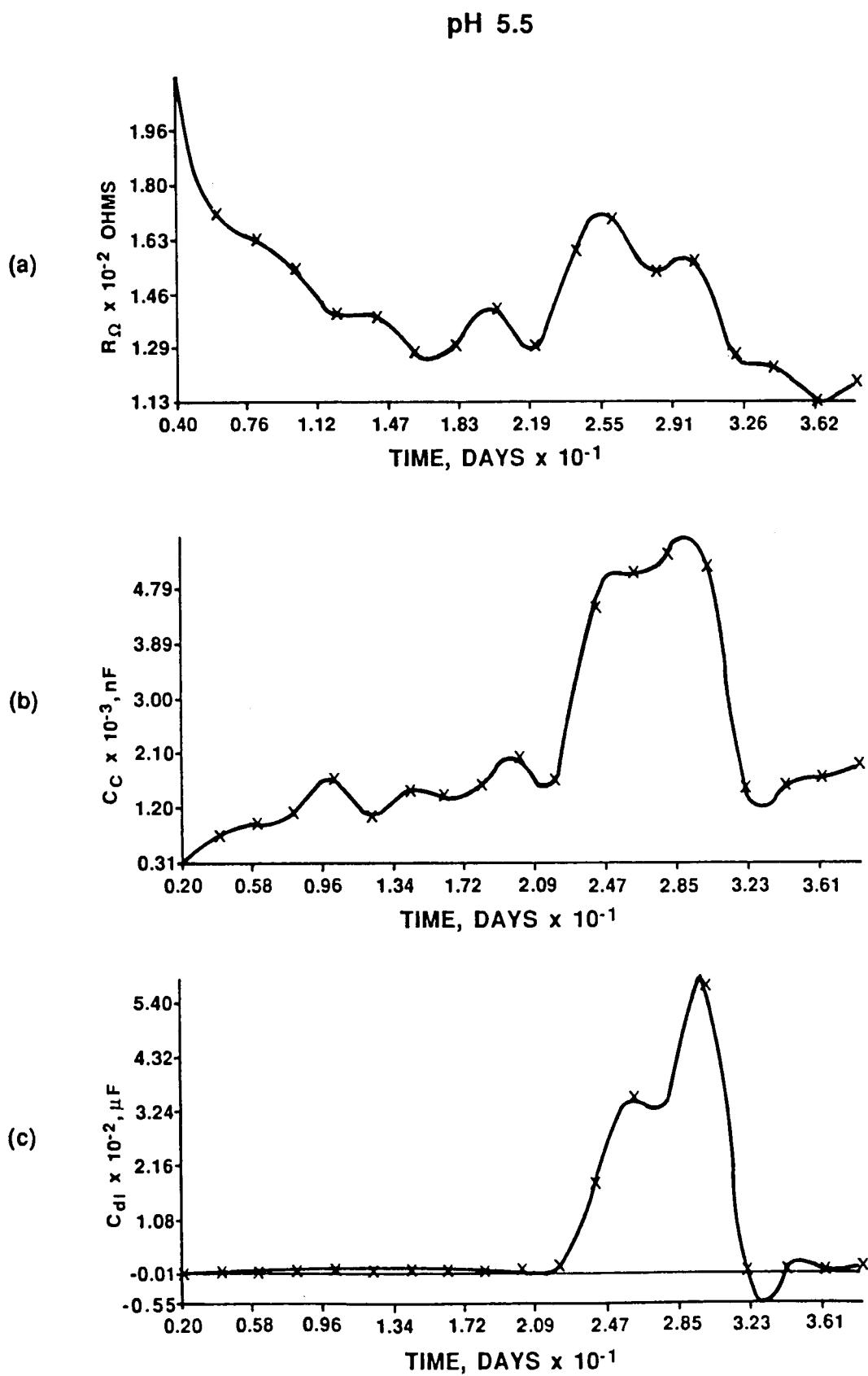


Figure 11. R_Ω , C_c , and C_{dl} versus time at pH 5.5.

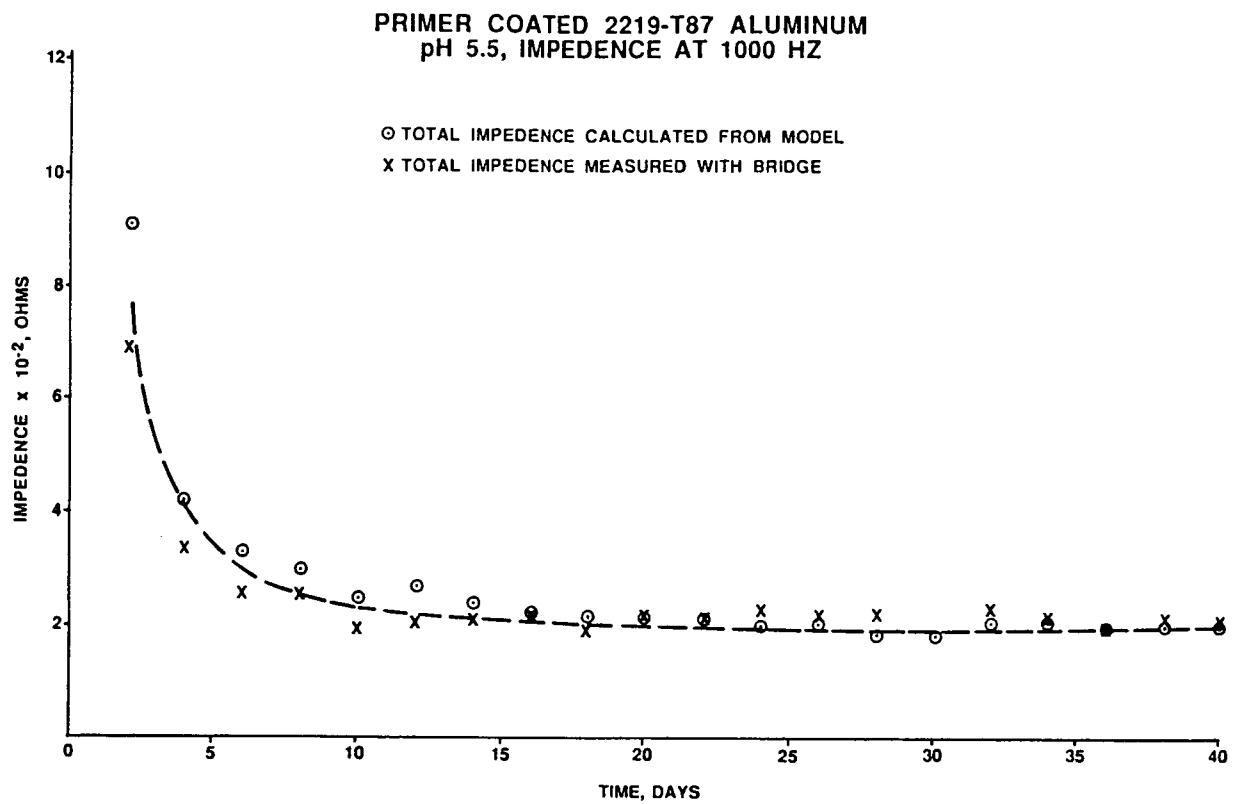


Figure 12. Total impedance at 1000 Hz for primer coated 2210-T87 aluminum at pH 5.5.

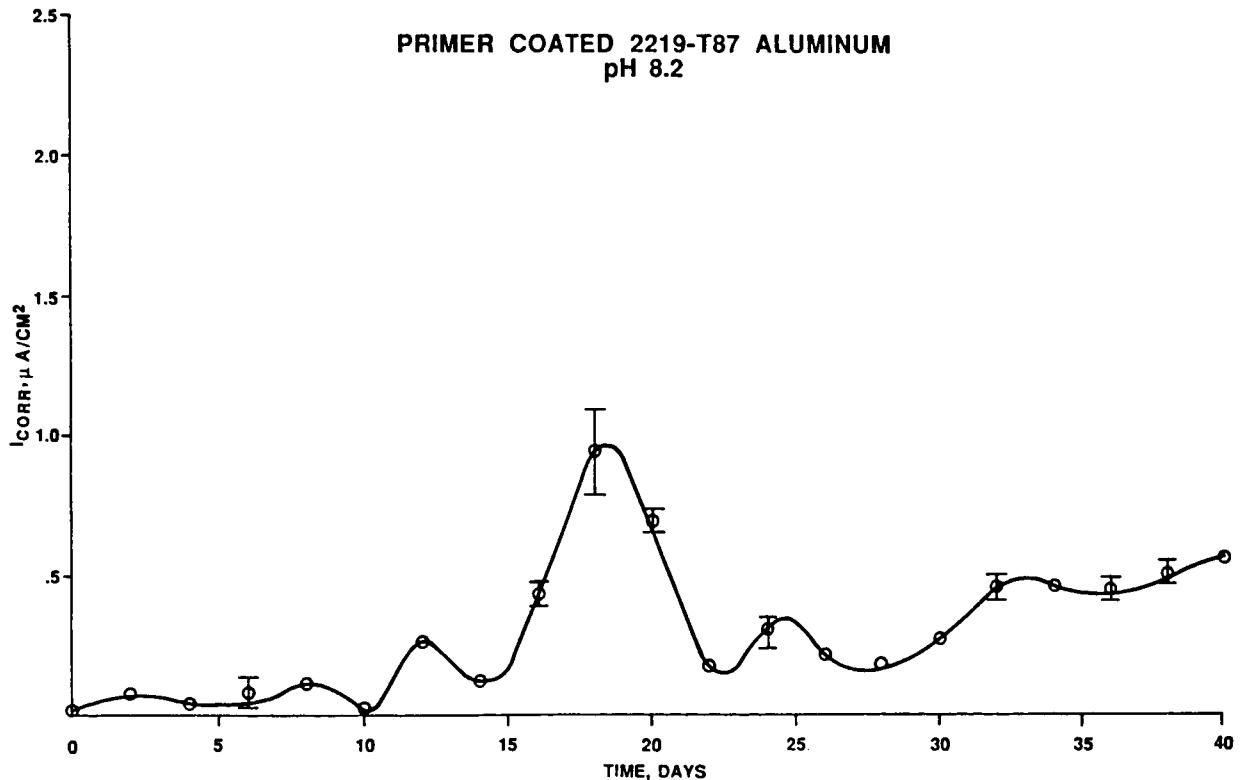


Figure 13. I_{CORR} versus time at pH 8.2 from polarization resistance measurements.

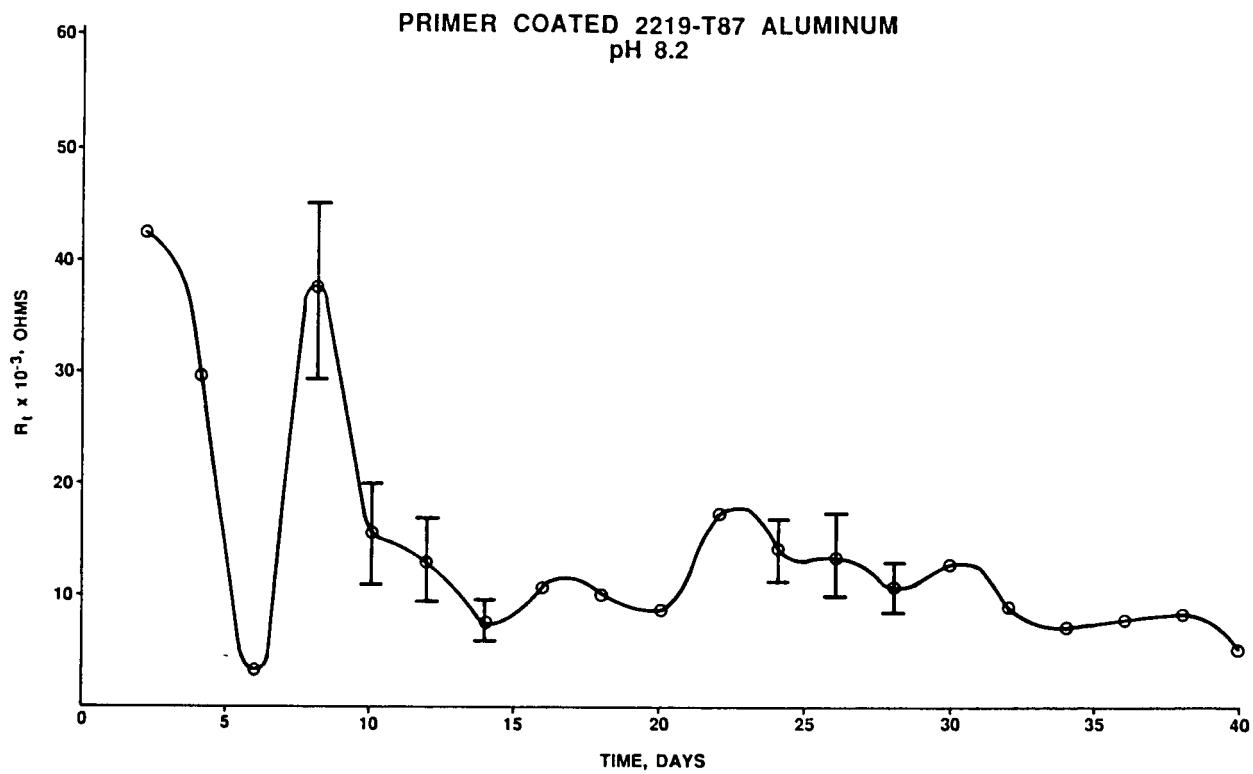


Figure 14. R_t versus time at pH 8.2.

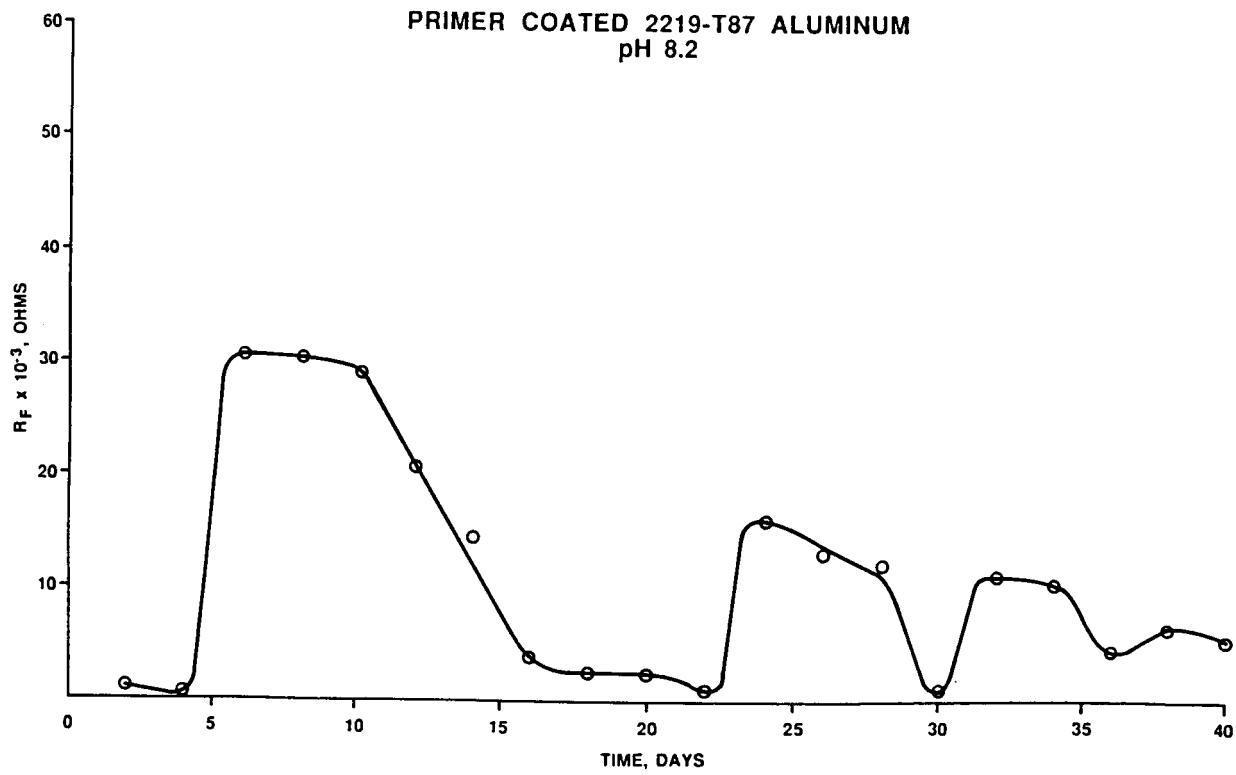


Figure 15. R_f versus time at pH 8.2.

far as the resistive components are concerned, has a relatively larger influence at pH 8.2 than at pH 5.5. In general, the R_f -time curve shows minimal values between 15 and 22 days, correlating well with the position of the main maximum in the I_{CORR} -time curve. Positions of maxima in the R_p -time curve [Fig. 16(a)] correlate well with the positions of maxima in the R_f -time curve and again suggest that the resistance of the paint film, probably associated with the buildup of corrosion products, plays an important role in the charge transfer between the paint film and solution. The C_s -time curve [Fig. 16(e)] shows little structure, but is generally increasing. Positions of maxima in the C_f -time curve [Fig. 16(b)], C_c -time curve [Fig. 17(b)], and C_{dl} -time curve [Fig. 17(c)] all correlate well with the positions of maxima in the R_f -time curve. The major peak in the I_{CORR} -time curve at pH 8.2 occurs at 18 days where the resistive components from the AC Impedance analyses exhibit minimum values. Values for R_∞ are again small, as for pH 5.5. A comparison of the total impedance at 1000 Hz with values measured with an AC impedance bridge at pH 8.2 is made in Figure 18.

CONCLUSIONS

The influence of the surrounding medium in the corrosion of primer coated aluminum is established by this study. Analysis of AC Impedance data clearly indicated that the charge transfer mechanism was predominant in the kinetics at both pH 5.5 and pH 8.2. The shapes of the I_{CORR} -time curves, as obtained using the DC polarization resistance technique, are clearly different at pH 5.5 and pH 8.2. These shapes correlate well with results from the AC Impedance technique, which is of great value in providing further insight into corrosion mechanisms. At pH 5.5, the corrosion rate is dominated by changes in the charge transfer resistance alone, although other resistive and capacitive effects are important during certain time periods as discussed previously.

At pH 8.2, both R_t and R_f contribute significantly, but changes in the R_t -time curve at smaller times are largely damped by increases of R_f in the R_f -time curve except at 18 days, where all components exhibit minimum values. It is significant that values for capacitative components are larger for short times at pH 8.2 than at pH 5.5, indicating that the barrier layer of Al_2O_3 may be thinner at this pH. Also changes in values of the resistive components at this pH are smaller. It is also significant that maxima and minima in the R_p -time curves at both pH levels correlate well with positions of similar maxima and minima in the charge transfer parameters between the paint film and solution. Increases in R_p are probably associated with a buildup of corrosion products within the paint film. From the shapes of the R_p -time curves at both pH levels, it seems that the corrosion products might be dissolved more rapidly at pH 5.5 than at pH 8.2. Although the positions of minima in the AC R_t -time and R_f -time curves are probably correlated with the onset of the hydrogen evolution reaction, which is in turn affected by oxygen diffusion, no additional information on this aspect of the corrosion mechanism was obtained from the AC Impedance technique.

This work, in general, confirms that AC Impedance measurements are of value in helping to determine corrosion mechanisms, and seems to indicate a good correlation between the behavior of AC Impedance and DC measurements with time for primer coated aluminum.

The resistive curves of the AC Impedance studies seem to correlate best with the DC curves. This probably results from the fact that, as the frequency of the alternating current approaches zero, DC type behavior of the circuit is obtained and thus only the resistive components are responsible for circuit behavior.

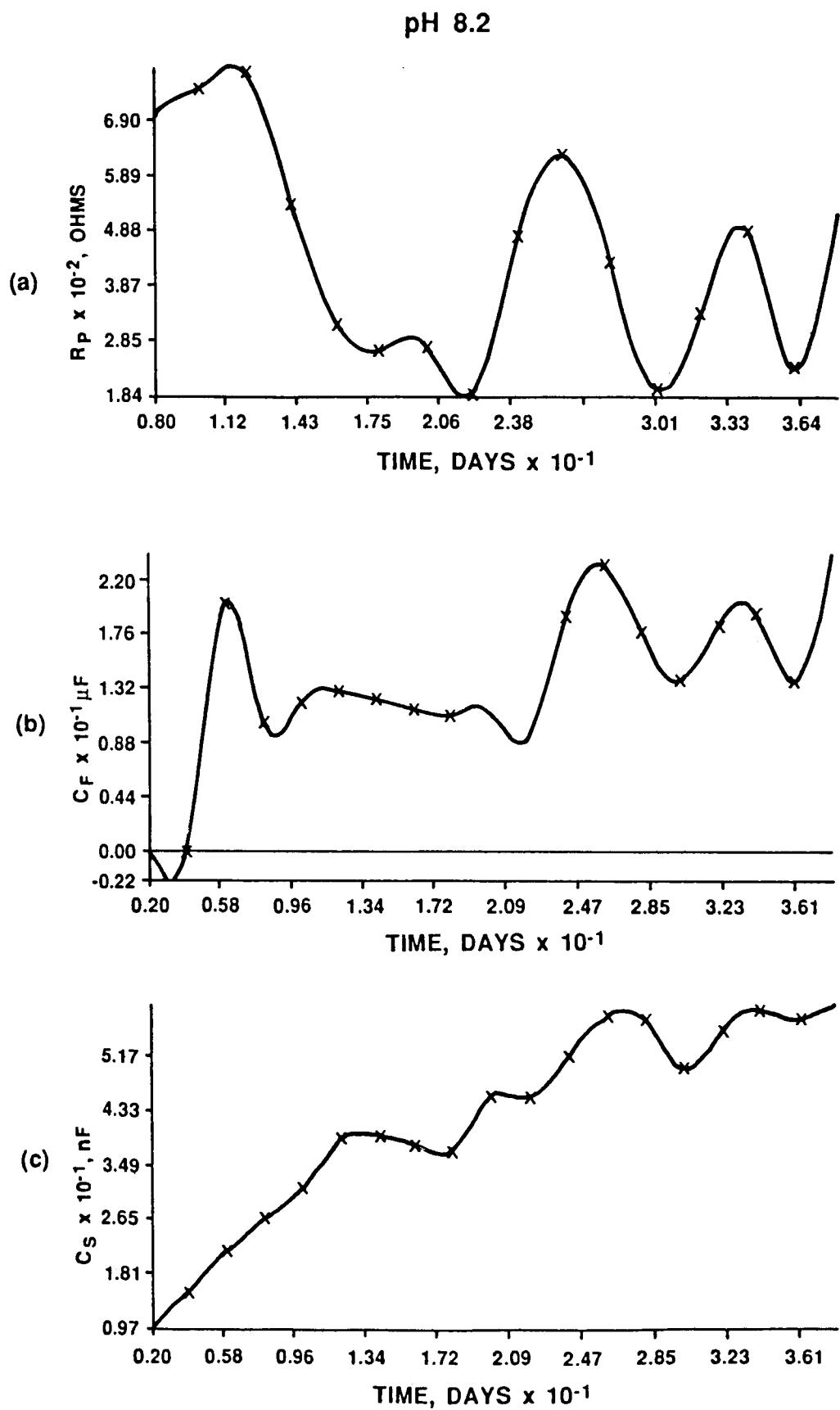


Figure 16. R_p , C_f , and C_s versus time at pH 8.2.

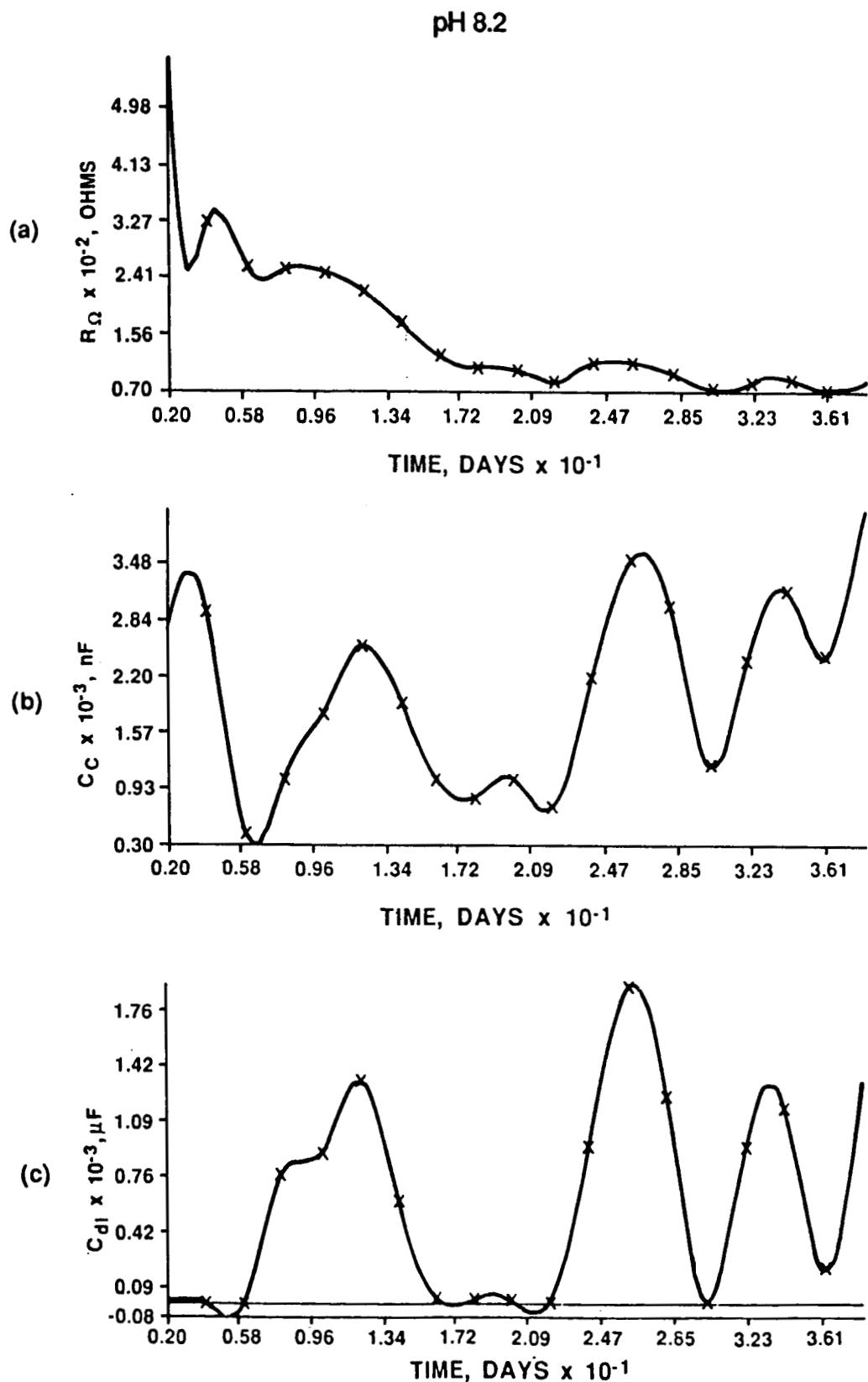


Figure 17. R_Ω , C_c , and C_{dl} versus time at pH 8.2.

PRIMER COATED 2219-T87 ALUMINUM
pH 8.2, IMPEDANCE AT 1000 Hz

O TOTAL IMPEDANCE CALCULATED FROM MODEL

X TOTAL IMPEDENCE MEASURED WITH BRIDGE

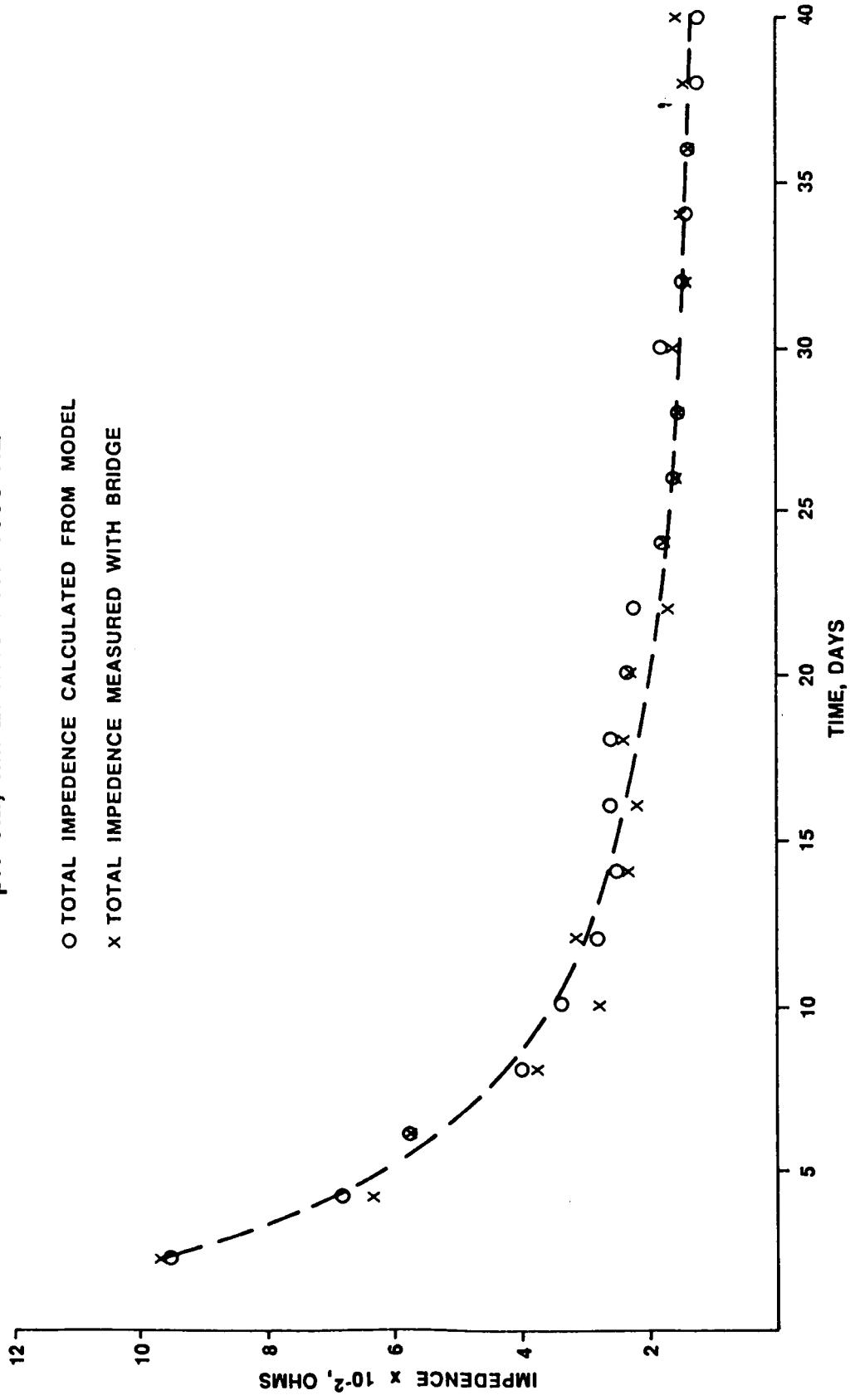


Figure 18. Total impedance at 1000 Hz for primer coated 2219-T87 aluminum at pH 8.2.

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1. REPORT NO. NASA TP-2715	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE The Corrosion Mechanisms for Primer Coated 2219-T87 Aluminum		5. REPORT DATE April 1987
7. AUTHOR(S) Merlin D. Danford and Ward W. Knockemus		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		8. PERFORMING ORGANIZATION REPORT #
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		10. WORK UNIT NO. M-559
		11. CONTRACT OR GRANT NO.
		13. TYPE OF REPORT & PERIOD COVERED Technical Paper
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

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Prepared by Materials and Processes Laboratory, Science and Engineering Directorate

16. ABSTRACT

In an effort to investigate metal surface corrosion and the breakdown of metal protective coatings, the AC Impedance Method was applied to zinc chromate primer coated 2219-T87 aluminum. The EG&G-PARC Model 368 AC Impedance Measurement System, along with DC measurements with the same system using the Polarization Resistance Method, was used to monitor changing properties of coated aluminum disks immersed in 3.5 percent NaCl solutions buffered at pH 5.5 and pH 8.2 over periods of 40 days each.

The corrosion system can be represented by an electronic analog called an equivalent circuit that consists of resistors and capacitors in specific arrangements. This equivalent circuit parallels the impedance behavior of the corrosion system during a frequency scan. Values for resistances and capacitances, that can be assigned in the equivalent circuit following a least squares analysis of the data, describe changes that occur on the corroding metal surface and in the protective coatings.

A suitable equivalent circuit has been determined that predicts the correct Bode phase and magnitude for the experimental sample. DC corrosion current density data are related to equivalent circuit element parameters.

17. KEY WORDS Electrochemical methods Primer-coated aluminum AC impedance technique Polarization resistance method Corrosion mechanism for primer-coated aluminum Correlation between AC and DC methods	18. DISTRIBUTION STATEMENT Unclassified - Unlimited
19. SECURITY CLASSIF. (of this report) Unclassified	
20. SECURITY CLASSIF. (of this page) Unclassified	
21. NO. OF PAGES 25	22. PRICE A02
Subject Category 26	